

# A kinetic study on decomposition of proton-bound dimer using data obtained by ion mobility spectrometry



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## ABSTRACT

In this study, an equation for measuring the rate constant of the proton-bound dimer decomposition reaction was derived using the data obtained by ion mobility spectrometry (IMS) technique. The ion mobility spectra of cyclohexanone (as the test compound) were obtained at various temperatures and different electric fields. The applied electric field for each temperature was varied between 375 and 500 V cm<sup>-1</sup> and the rate constant values of 188.24, 180.54, 280.64, 288.34 and 379.60 s<sup>-1</sup> were obtained at different temperatures of 463, 468, 473, 478 and 483 K, respectively. Subsequently, the activation energy and pre-exponential factor were calculated to be 69.5 kJ mol<sup>-1</sup> and  $1.2 \times 10^{10}$  s<sup>-1</sup>, respectively. In addition, the standard enthalpy changes were calculated for the dimer decomposition reaction of cyclohexanone at the above-mentioned temperatures.

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## 1. Introduction

Systematic studies of the reactions of positive and negative ions with molecules in the gas phase were initiated in the early 1950s [1]. Ion–molecule reactions can supply key information to help recognize the essential factors that determine gas-phase ion structures [2]. Hundreds of research groups with a wide variety of scientific interests ranging from chemical physics to biochemistry have contributed to the extensive literature in the field of gas-phase ion chemistry [3–5]. The proton transfer reactions, a group of ion–molecule reactions, are carried out in biological and chemical processes. To date, a lot of theoretical and experimental studies have been performed to provide and enrich the specialized information regarding the possible mechanisms of proton transfer and relevant properties associated with proton transfer [6–10]. Yet, there seems to be a gap which needs to be filled. Thus to study the ion–molecule reactions comprehensively, an investigation of their kinetics and thermodynamics appears essential. Kinetic study of the ion–molecule reactions is more difficult than that for neutral–neutral reactions due to the high-rate nature of the ion–molecule reactions. Commonly, several techniques such as high pressure mass spectrometry (HPMS) [11,12], flowing afterglow (FA) [13,14], selected ion flow tube (SIFT) [15,16], ion cyclotron resonance spectrometry (ICR) [17,18] and ion mobility spectrometry (IMS) [3,19–22] have been used for measuring the rate constant

of ion–molecule reactions. As we know, the methods of HPMS, FA, SIFT, and ICR entail the functioning pressures less than about 6 Torr, which would make it difficult to conduct experiments. However, ion mobility spectrometry technique can be used at atmospheric pressure [19]. To date, IMS has been used as an acceptable method for the identification and quantification of trace compounds such as explosives, chemical weapons and illicit drugs [19]. This technique has also been used for the kinetic study of various gas-phase ion–molecule reactions at atmospheric pressure [23–26]. In fact, scientists have been encouraged to employ this technique since it enjoys certain important advantages including portability, low cost, high speed, ease of maintenance, and high sensitivity. In ionization region of IMS, the protonated molecules (MH<sup>+</sup>) of the sample (M), named monomers, could be produced through abstracting protons from the reactant ions ((H<sub>2</sub>O)<sub>n</sub>H<sup>+</sup> + M → MH<sup>+</sup> + nH<sub>2</sub>O). By increasing the sample concentration, monomer ions can also react with the neutral sample molecules, and as a result, dimer ions (MH<sup>+</sup>M) can be formed (MH<sup>+</sup> + M → MH<sup>+</sup>M) [27]. The kinetics of proton-bound dimer decomposition has been studied by Ewing et al. [21] using IMS with <sup>63</sup>Ni ionization source (<sup>63</sup>Ni-IMS). They measured the rate constant for the dissociation of dimer to monomer ions for DMP (2,4-dimethyl pyridine) and DMMP (dimethyl methyl phosphonate). In 2009, we proposed a method to be employed in the study of the kinetic of proton-bound dimer formation and for the measurement of the rate constants in the formation reaction using corona discharge ion mobility spectrometry (CD-IMS) [22]. The method was evaluated using the same compounds as those studied by Ewing et al. [21]. <sup>63</sup>Ni provides a

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stable production of ions without an extra power source, but a regular leak test is required due to its radioactive property. Therefore, there is an increasing interest in replacing radioactive sources by nonradioactive ones. The corona discharge ionization source is a good choice for producing the ions from analytes in IMS [28]. The major advantage of this ionization source over  $^{63}\text{Ni}$  is a higher total ion current by about an order of magnitude. This ensures a better sensitivity, a higher signal-to-noise ratio, and a wider working range [29].

In this study, an equation was derived for measuring the rate constant of the decomposition reaction of proton-bound dimer using the spectra obtained by CD-IMS technique. This method was practically scrutinized and validated for cyclohexanone as the test compound. The activation energy, pre-exponential factor, and the standard enthalpy change for the decomposition reaction of proton-bound dimer were calculated.

## 2. Experimental section

### 2.1. Instrumentation

In this work, corona discharge ionization ion mobility spectrometry (CD-IMS) was used for measuring the decomposition reaction rate constant of cyclohexanone dimer. The instrumentation of this apparatus can be found in the work reported previously by Tabrizchi et al. [29]. Briefly, the IMS cell is divided into the ionization and drifting regions, separated by a shutter grid. The grid potential is removed for a short period of time (typically 200  $\mu\text{s}$ ) by the pulse generator, to admit an ion pulse to the drift region. The external electric field will be recognized within the drift tube using several drift rings for stabilization. In this work, the ion mobility spectrometer was utilized with various drift fields ranging from 375 to 500  $\text{V cm}^{-1}$ . The ionization of the chemical compounds occurs by application of continuous corona discharge ionization source. A drift gas (nitrogen) will flow from the Faraday plate towards the ionization region. In this work, the sample vapor was entered into the sample introduction system of instrument by a syringe pump (SP1000, Fanavaran Co. Iran) with various speeds. Nitrogen gas was also used as carrier gas, helping to transfer the sample vapor into the ionization region of IMS cell.

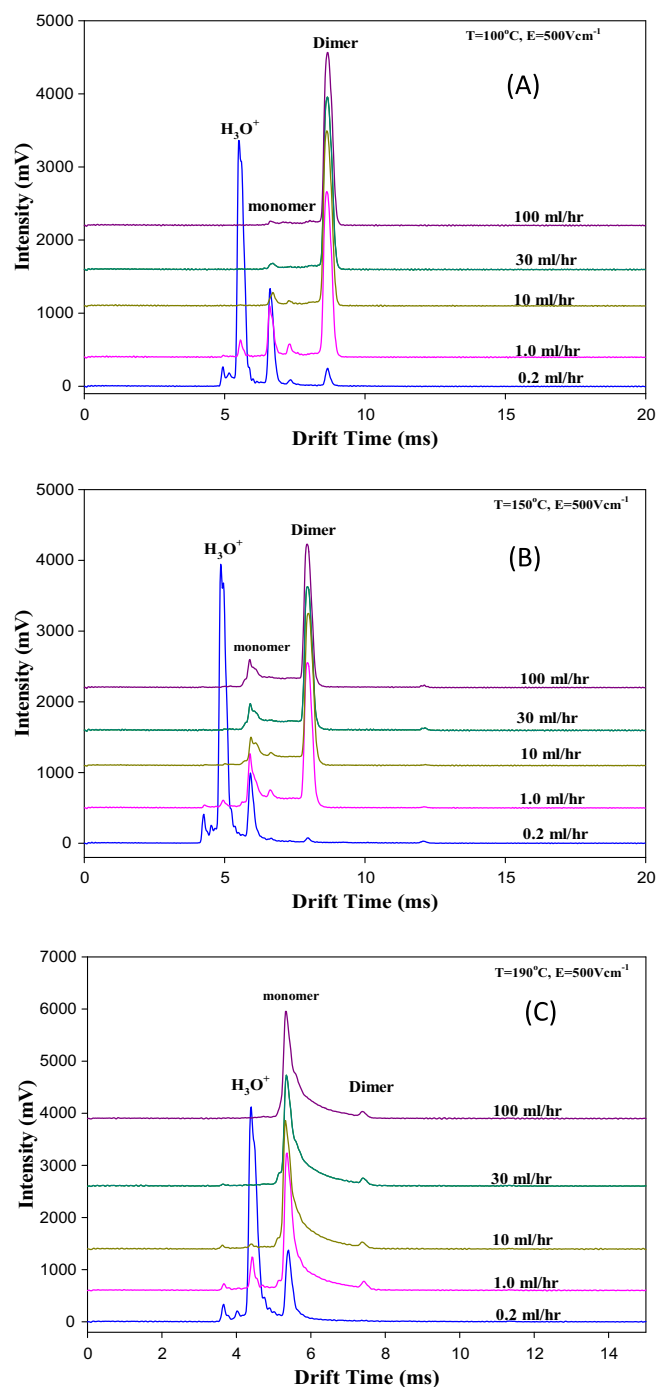
### 2.2. Calculation of sample concentration

The chemical used in this study was cyclohexanone (99%) purchased from Merck ( $d = 0.947 \text{ g mL}^{-1}$ ). Cyclohexanone headspace was sampled by using a 10-mL syringe at laboratory temperature (26 °C). To calculate the cyclohexanone headspace concentration, the equation of state of ideal gas was employed. Using the vapor pressure of cyclohexanone at 26.4 °C (5 mm-Hg) [30], the concentration of the sample in its headspace was calculated to be  $2.68 \times 10^{-4} \text{ mol L}^{-1}$ . In the next step, the concentration of the sample in the ionization region was determined using the flow rate of the carrier gas as well as the sample vapor flow. At various temperatures, the appropriate concentration of the sample in the ionization region was achieved by adjusting the rate of the syringe pump. The pumping speed was considered suitable when a stable tail was observed between the monomer ( $\text{MH}^+$ ) and dimer ( $\text{MH}^+\text{M}$ ) peaks in ion mobility spectrum.

## 3. Results and discussion

### 3.1. Concentration and temperature effects

Fig. 1 depicts the effect of concentration on the ion mobility spectra of cyclohexanone in the electric field of  $500 \text{ V cm}^{-1}$ . These



**Fig. 1.** The effect of concentration on mobility spectrum of cyclohexanone ( $2.68 \times 10^{-4} \text{ mol L}^{-1}$  in headspace sample), (A): 100 °C, (B): 150 °C and (C): 190 °C. The flow rates of drift gas and carrier gas were 700 and 300  $\text{mL min}^{-1}$ , respectively.

spectra were obtained at different drift tube temperatures of 100, 150 and 190 °C. When the sample is introduced into the ionization region, an ion–molecule reaction could occur by a competitive proton transfer between the reactant ions ( $(\text{H}_2\text{O})_n\text{H}^+$ ) and sample molecules (M). Under suitable conditions, the protonated molecules of the sample, named monomers ( $\text{MH}^+$ ), could be produced ( $(\text{H}_2\text{O})_n\text{H}^+ + \text{M} \rightarrow \text{MH}^+ + n\text{H}_2\text{O}$ ). By increasing the sample concentration, monomer ions can also react with the sample molecules, and as a result, proton bound dimer ( $\text{MH}^+\text{M}$ ) can be formed ( $\text{MH}^+ + \text{M} \rightarrow \text{MH}^+\text{M}$ ). As can be seen in Fig. 1(A), at the low rate

of the syringe pump ( $0.2 \text{ mL h}^{-1}$ ), where the concentration of cyclohexanone is not high, a dimer peak with low intensity can be observed in addition to a considerable monomer ion peak. By enhancing the sample concentration inside the ionization region, the intensity of dimer is increased. However, as expected, the intensity of monomer ions is diminished by increasing the injection speed as they change into dimer form. At  $100 \text{ mL h}^{-1}$  injection rate, the monomer peak completely disappears. Fig. 1(B) and (C) shows the same investigation at higher temperatures of 150 and  $190^\circ\text{C}$ , respectively. It is evidently observed that increasing the temperature can prevent the formation of dimer. As can be seen, ion mobility spectra in Fig. 1(A) and (B) shows that in the same concentrations, lower amounts of monomer and dimer are formed at  $150^\circ\text{C}$  compared to  $100^\circ\text{C}$  simply because association reactions are exothermic. Fig. 1(C) shows that the created dimer ions are rapidly converted to the monomers at  $190^\circ\text{C}$  and hence, a considerable tailing can be observed between the monomer and dimer peaks. In fact, tail formation is accomplished due to the dissociation of dimer ions at different distances from drift tube with high temperature. For more investigation, the ion mobility spectra of the sample with low concentration ( $0.2 \text{ mL h}^{-1}$ ) and high concentration ( $100 \text{ mL h}^{-1}$ ) at various temperatures are shown in Fig. 2(A) and (B), respectively. As Fig. 2(A) shows, at low concentration of the sample, dimer peak can be seen only at the temperature of  $100^\circ\text{C}$  and it disappears by increasing the temperature to higher than  $150^\circ\text{C}$ . On the other hand, Fig. 2(B) shows in high concentration sample, all of the reactant ions and monomer ions react with the sample at  $100^\circ\text{C}$ , and consequently, their peaks disappear and only dimer peak can be seen. Therefore, as some monomer ions are retained in the reaction region at high temperatures, both the monomer and dimer peaks are observed in the mobility spectrum. As illustrated in Fig. 1(C), the created dimer ions are rapidly converted to the monomers at  $190^\circ\text{C}$  and hence, a considerable tailing can be observed between the monomers and dimer peaks.

### 3.2. Deriving the equation

For measuring the rate constant of the decomposition reaction of dimer ions, it is necessary to obtain distribution of dimer ions in the drift region. In this regard, reaction (1) was considered.



Then, rate equation of reaction (1) was written as:

$$\frac{d[\text{MH}^+\text{M}]}{dt} = -k_{-2}[\text{MH}^+\text{M}] + k_2[\text{MH}^+][\text{M}] \quad (2)$$

Since, the decomposition reaction of dimer ions is endothermic, the forward reaction (formation reaction of dimer ions) can be ignored at high temperatures. In this case, the forward reaction cannot take place because the sample molecule (M) produced from the decomposition of dimer ions is separated from the monomer ions by the drift gas flow. In our previous work<sup>22</sup>, we scrutinized dimer formation reaction carefully at low temperatures for measuring  $k_2$  for DMP and DMMP. In this work, we study reaction (1) at high temperature for measuring  $k_{-2}$  using CD-IMS. Thus:

$$\frac{d[\text{MH}^+\text{M}]}{dt} = -k_{-2}[\text{MH}^+\text{M}] \quad (3)$$

By integration of Eq. (3), we obtained:

$$[\text{MH}^+\text{M}]_t = [\text{MH}^+\text{M}]_0 \exp(-k_{-2}t) \quad (4)$$

where  $[\text{MH}^+\text{M}]_0$  is initial concentration of dimer ions packet passed from shutter grid and  $[\text{MH}^+\text{M}]_t$  is concentration of dimer ions packet at elapsed time,  $t$ , in the drift tube. By considering  $X$  and  $V_D$  equal to the distance traveled by dimer ions in the drift region, and speed of these ions, respectively, we can write:

$$X = V_D t \quad (5)$$

Then, substituting  $t$  from Eq. (5) in Eq. (4) yields:

$$[\text{MH}^+\text{M}]_X = [\text{MH}^+\text{M}]_0 \exp\left(-k_{-2} \frac{X}{V_D}\right) \quad (6)$$

It must be noted that  $[\text{MH}^+\text{M}]_X$  is the concentration of dimer ions packet at different distances from the shutter grid in the drift region. Since collision of ions with the collector in the IMS produces electric current ( $i$ ), we have:

$$i_D = [D]V_D \quad (7)$$

where,  $i_D$  is dimer ionic current and  $[D]$  is dimer ions density  $\left(\frac{dN_D}{dX}\right)$ . Therefore, number of dimer ions at  $X=0$  is equal to:

$$(N_{\text{MH}^+\text{M}})_0 = [D]_0 V_D dt \quad (8)$$

$V_D dt$  is equal to  $dX$  and expresses dimer ions packet introduced into the drift region with speed of  $V_D$  has  $dt$  width. If Eq. (6) is substituted based on the numbers of dimer ions, it can be written as:

$$(N_{\text{MH}^+\text{M}})_X = (N_{\text{MH}^+\text{M}})_0 \exp\left(-k_{-2} \frac{X}{V_D}\right) \quad (9)$$

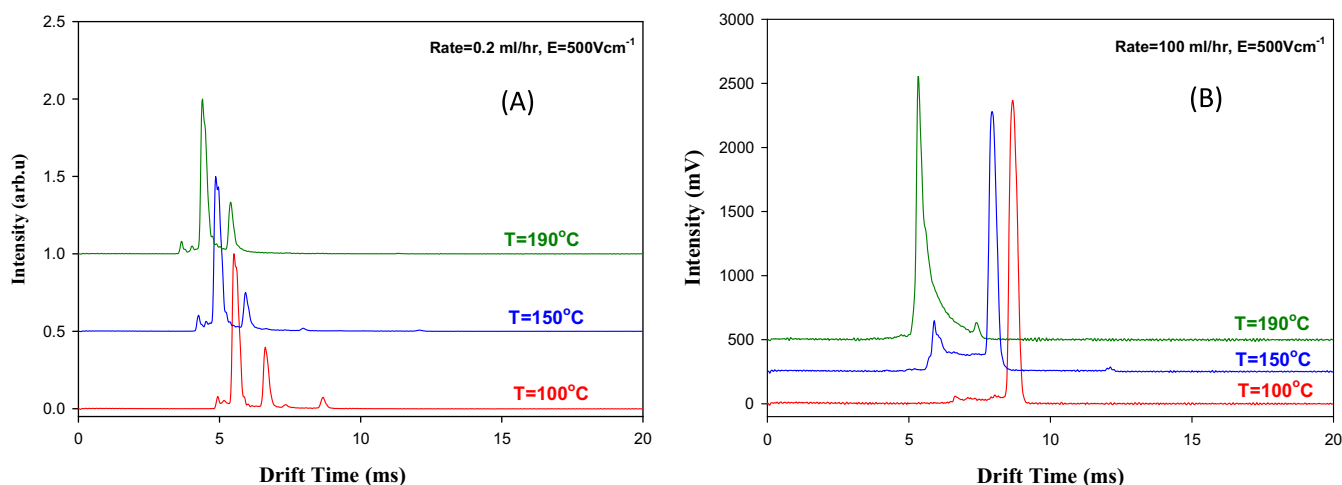


Fig. 2. The effect of temperature on the mobility spectrum of cyclohexanone ( $2.68 \times 10^{-4} \text{ mol L}^{-1}$  in headspace sample), (A):  $0.2 \text{ mL h}^{-1}$  and (B):  $100 \text{ mL h}^{-1}$ . The flow rates of drift gas and carrier gas were 700 and  $300 \text{ mL min}^{-1}$ , respectively.

By substituting Eq. (8) in Eq. (9) and using Eq. (7),  $i_D$  is obtained:

$$i_D = -k_{-2}[D]_0 V_D dt \exp\left(-k_{-2} \frac{X}{V_D}\right) \quad (10)$$

Since  $dt$  as the width of dimer ions packet traveled in the drift region is taken to be  $t_g$  (width of pulse applied to the shutter grid), thus:

$$i_D = -k_{-2}[D]_0 V_D t_g \exp\left(-k_{-2} \frac{X}{V_D}\right) \quad (11)$$

Eq. (11) presents the distribution of the dimer ions in the drift tube at different distances from shutter grid. This equation should be varied to the time domain because of the signal being versus time in the IMS. In this regard,  $L$  is considered the length of drift tube and  $X$  and  $L - X$  designate the distances that ion moves as the dimer ion and as the monomer ion, respectively. Therefore, the elapsed time by the ion in the drift region can be obtained by:

$$t = \frac{X}{V_D} + \frac{L - X}{V_M} \quad (12)$$

where,  $V_M$  is the speed of the monomer ions. This equation shows that if dimer ion is decomposed to monomer ion at  $X = 0$ , it results in  $t = t_M$  (drift time of the monomer peak). And if it happens at  $X = L$ ,  $t$  corresponds to the drift time of the dimer peak,  $t_D$ . So, the decomposition of dimer ion between  $X = 0$  and  $X = L$  constructs a tail between monomer and dimer peaks. By plugging  $X$  obtained from Eq. (12) into Eq. (11), we can write:

$$i_D = -k_{-2}[D]_0 V_D t_g \exp\left(-k_{-2} \frac{t_D(t - t_M)}{(t_D - t_M)}\right) \quad (13)$$

And therefore,

$$\ln i_D = \ln(-k_{-2}[D]_0 V_D t_g) + \frac{k_{-2} t_D t_M}{t_D - t_M} - \frac{k_{-2} t_D t}{t_D - t_M} \quad (14)$$

As Eq. (14) shows, when the logarithm of the tail intensity is plotted versus drift time, the plot slope is proportional to the rate constant. Hence, by substituting the drift time of dimer and monomer ions in the slope of Eq. (14),  $k_{-2}$  can be obtained.

### 3.3. Practical evaluation of the derived equation

To demonstrate the capability of the proposed method for measuring the rate constant of dimer decomposition, cyclohexanone

was selected as a test compound. Fig. 3 shows the ion mobility spectra of this compound in different drift fields (375–500  $\text{V cm}^{-1}$ ) and at the temperature of 478 K. As mentioned in Section 3.1, at high concentration of the sample in the ionization region, no reactant ions survive and only monomer and dimer ions are present. In addition, as can be obviously observed in Fig. 1(C) and Fig. 3, a tail between monomer and dimer peaks would be formed due to the decomposition of dimer. This phenomenon can occur at different distances from shutter grid, through the drift tube. Because the decomposition of dimer is an endothermic reaction, the reaction can be processed by increasing the temperature. The suitable temperature range for the generation of a tail between monomer and dimer peaks at the decomposition reaction of cyclohexanone dimer is 463–483 K. Fig. 4 depicts the plots of the tail intensity logarithm versus drift time at 478 K in different drift fields. In fact, the data correspond to the region between monomer and dimer peaks (tail) in ion mobility spectra (shown in Fig. 3) was selected for constructing of Fig. 4. As indicated in Fig. 4, all the plots are linear and parallel. Therefore, it can be easily concluded from Eq. (14) that the slopes of these plots are equal to  $\frac{k_{-2} t_D}{t_D - t_M}$ . In this relation,  $t_M$  and  $t_D$  are dependent on drift field. However, the ratio of  $\frac{t_D}{t_D - t_M}$  is independent relative to this variable. The results obtained for  $k_{-2}$  at various temperatures and different drift fields are tabulated in Table 1. As shown in this Table, the values of  $k_{-2}$  obtained for different drift fields are almost close to each other, for each temperature. Therefore,  $k_{-2}$ , 188.24, 180.54, 280.64 and 288.34, and 379.60  $\text{s}^{-1}$  were calculated from the average of the obtained results in various electric fields for 463, 468, 473, 478, and 483 K. To date, the rate constant of cyclohexanone dimer decomposition using IMS and other methods has not been reported. However, the rate constants in the order of  $10^2 \text{ s}^{-1}$  have already been observed for the first-order dissociation reactions [21,31], indicating an acceptable agreement with our results.

### 3.4. Calculation of activation energy

In this work, the rate constants were measured in a narrow range of temperatures, Therefore, the Arrhenius equation can be used for calculation of the activation energy and pre-exponential factor.

$$\ln k = \ln A - \frac{E_a}{RT} \quad (15)$$

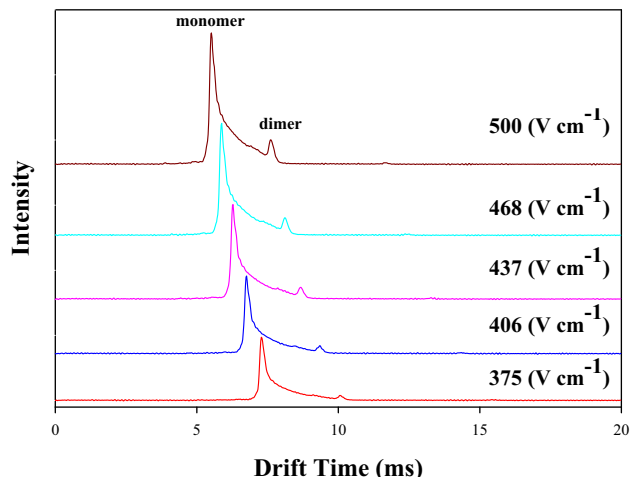


Fig. 3. Ion mobility spectra of cyclohexanone ( $2.68 \times 10^{-4} \text{ mol L}^{-1}$  in headspace sample) at different drift fields and at the temperature of 478 K. The flow rates of drift gas and carrier gas were 700 and 300  $\text{mL min}^{-1}$ , respectively.

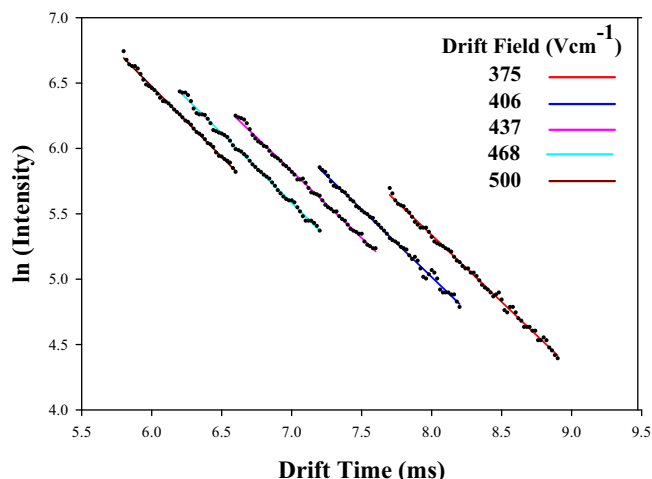


Fig. 4. Logarithm of the dimer ion intensity of tail at different drift fields at temperature of 478 K.

**Table 1**

Rate constant of cyclohexanone dimer decomposition at various temperatures and drift fields.

Temperature (K)	Drift field (V cm <sup>-1</sup> )	$t_M \pm 0.02$ (ms)	$t_D \pm 0.02$ (ms)	Slope	$k_{-2}$ (s <sup>-1</sup> )
463	375	7.42	10.22	$-0.6542 \pm 0.0150$	$188.24 \pm 7.05$
	406	6.86	9.46	$-0.6794 \pm 0.0089$	
	437	6.40	8.80	$-0.7139 \pm 0.0098$	
	468	5.97	8.22	$-0.6933 \pm 0.0081$	
	500	5.62	7.72	$-0.7150 \pm 0.0124$	
468	375	7.42	10.24	$-0.6598 \pm 0.0094$	$180.54 \pm 1.59$
	406	6.86	9.47	$-0.6773 \pm 0.0111$	
	437	6.46	8.82	$-0.6698 \pm 0.0102$	
	468	6.02	8.24	$-0.6654 \pm 0.0089$	
	500	5.62	7.76	$-0.6623 \pm 0.0101$	
473	375	7.32	10.12	$-0.9945 \pm 0.0113$	$280.64 \pm 15.57$
	406	6.74	9.34	$-1.0608 \pm 0.0254$	
	437	6.36	8.74	$-1.0456 \pm 0.0107$	
	468	5.92	8.12	$-0.9235 \pm 0.0083$	
	500	5.52	7.64	$-1.0454 \pm 0.0186$	
478	375	7.32	10.12	$-1.0234 \pm 0.0076$	$288.34 \pm 6.33$
	406	6.84	9.34	$-1.0326 \pm 0.0103$	
	437	6.34	8.72	$-1.0261 \pm 0.0076$	
	468	5.96	8.16	$-1.0615 \pm 0.0078$	
	500	5.57	7.62	$-1.0787 \pm 0.0101$	
483	406	6.72	9.34	$-1.3894 \pm 0.0135$	$379.60 \pm 11.95$
	437	6.24	8.62	$-1.3311 \pm 0.0099$	
	468	5.86	8.12	$-1.3283 \pm 0.0091$	
	500	5.52	7.64	$-1.4129 \pm 0.0114$	

The values of  $\ln k_{-2}$  were obtained 5.24, 5.20, 5.64, 5.66, and 5.94 at different temperatures of 463, 468, 473, 478, and 483 K, respectively. Fig. 5 depicts the plot of  $\ln k_{-2}$  versus  $1/T$ , showing a linear relationship between them. According to Arrhenius equation, the slope is equal to  $\frac{E_a}{R}$ . On the other hand, the intercept of the plot corresponds to  $\ln A$ .

The activation energy and the natural logarithm of pre-exponential factor were determined to be  $69.5 \pm 4.9$  kJ mol<sup>-1</sup> and  $23.21 \pm 3.65$ , respectively.

### 3.5. Calculation of the standard enthalpy change

As the activation energy of the formation reaction of dimer is approximately zero, the standard enthalpy change for the dissociation reaction of dimer can be calculated from Eq. (16). This corresponds to general understanding about ion–molecule reactions [21,22]. In the previous work [22], we calculated the activation energy of the dimer formation reaction for DMP and DMMP. The results indicated that no activation energy was involved in the formation of proton-bound dimers of DMP and DMMP.

**Table 2**

The standard enthalpy change of decomposition reaction of the cyclohexanone dimer at different temperatures.

Temperature (K)	Standard enthalpy change (kJ mol <sup>-1</sup> )
463	73.374
468	73.415
473	73.457
478	73.499
483	73.540

$$\Delta H_{\text{dissociation}} = E_{a\text{dissociation}} + RT \quad (16)$$

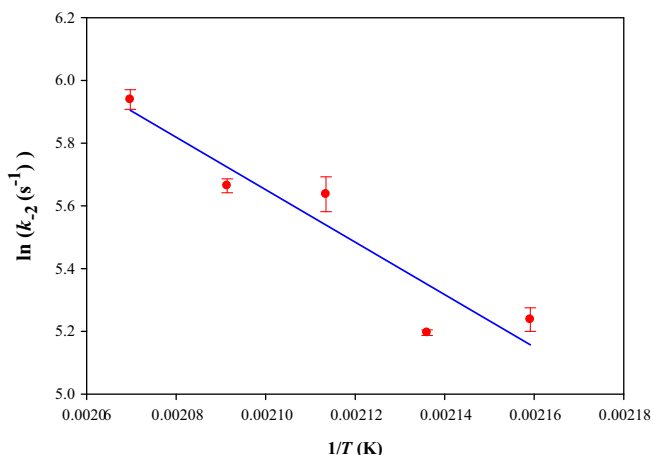
The results obtained for the standard enthalpy changes of the decomposition reaction of cyclohexanone dimer at different temperatures are shown in Table 2. As can be expected, the standard enthalpy change is increased by enhancing the temperature.

## 4. Conclusion

In this work, the corona discharge ion mobility spectrometry (CD-IMS) was used for kinetic study of ion–molecule reactions. The effects of analyte concentration and the cell temperature on the mobility spectra of cyclohexanone were investigated. A tail between monomer and dimer ion peaks is formed due to the dissociation of dimer ions at different distances from drift tube and at an appropriate temperature. In this study, a suitable equation was derived for distribution of dimer ions in the drift region, indicating that the slope of the logarithm of tail intensity versus drift time is proportional to rate constant of dimer decomposition. The rate constant, activation energy, pre-exponential factor, and the standard enthalpy change were all calculated for dimer decomposition of cyclohexanone (selected as the test compound). The appropriate results obtained in this work reveal the capability of CD-IMS for easy study of kinetic properties.

### Conflict of interest

No conflict of interest is with this paper.

**Fig. 5.** The plot of  $\ln k_{-2}$  versus  $1/T$ .



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